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金属卟啉存在下芳醛氧化反应的研究

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摘要 本文研究了在金属四苯基卟啉[Co(II)TPP,Fe(III)TPPCl,Mn(III)TPPCl,Zn(II)TPP,Cu(II)TP.TPP=四苯基卟啉]存在下,用氧气氧化芳醛的过程.测定了反应体系的吸氧动力学曲线;观察了氧化过程中金属卟啉的可见光谱的变化;研究了底物,金属卟啉在反应体系中的浓度以及溶剂等因素对反应的影响.结果发现,除能可逆键合分子氧的Co(II)TPP外,不具此种功能的Fe(III)TPPCl和Mn(III)TPPCl也能加速芳醛的氧化反应.然而,它们的催化作用是在金属四苯基卟啉与反应过程中积累起来的过酸作用,卟啉环遭到破坏后观察到的,此时可能形成了某种新的催化活性中心.金属卟啉本身对反应起抑制作用,它只是表观上的催化剂,其催化作用看来不应归结为对分子氧的活化.

关键词 卟吩 P 氧化 催化剂 锌络合物 铁络合物 铜络合物 钴络合物 醛 芳香族化合物 锰络合物

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Oxidation of aromatic aldehydes in the presence of metallotetraphenylporphyrins

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Abstract In the presence of metallotetraphenylporphyrins [(Co(II)TPP, Fe(III)TPPCl, Mn(III)TPPCl, Cu(II)TPP, and Zn(II)TPP, TPP = tetraphenylporphyrin], the oxidation of RC6H4CHO (R = H, 4-Cl) with mol. oxygen has been investigated. The oxygen uptake and changes in the electronic spectrum of metallotetraphenylporphyrins during the course of the reaction were measured. It was observed that besides Co(II)TPP that can reversibly bind mol. oxygen, Fe(III)TPPCl and Mn(III)TPPCl which are not capable of binding mol. oxygen reversibly can also catalyze the oxidation of aldehydes, while Cu(II)TPP and Zn(II)TPP are inactive. The oxidation reaction, however, is catalyzed by some catalytically active species which is formed from the interaction between metalloporphyrin and percarboxylic acid accumulated during the course of the reaction with the destruction of porphyrin ring, and is inhibited by the metalloporphyrin itself. In the reaction systems, the metalloporphyrins are nominal catalysts. It seems that the catalytic role of metallotetraphenylporphyrin in the oxidation of aromatic aldehydes should not be attributed to its capability of activating mol. oxygen.

Key words PORPHINE P OXIDATION CATALYST ZINC COMPLEX IRON COMPLEX COPPER COMPLEX COBALT COMPLEX ALDEHYDES AROMATIC COMPOUNDS MANGANESE COMPLEX

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